(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 6 December 2001 (06.12.2001)

PCT

(10) International Publication Number WO 01/92694 A1

(51) International Patent Classification7:

101

(21) International Application Number: PCT/KR01/00912

(22) International Filing Date: 31 May 2001 (31.05.2001)

(25) Filing Language:

English

F01N 3/20

(26) Publication Language:

English

(30) Priority Data:

2000/29869 2001/12180 1 June 2000 (01.06.2000) KR 9 March 2001 (09.03.2001) KR

(71) Applicant (for all designated States except US): BLUE PLANET CO., LTD. [KR/KR]; 131A, Yonsei Engineering Research Center, 134, Shinchon-Dong, Sudaemoon-ku, Seoul 120-749 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CHUN, Kwang, Min [KR/KR]; Jangmi Apt. 8-1106, Sincheon-dong, Songpa-Gu, Seoul 138-240 (KR). CHUN, Bae, Hyeock [KR/KR]; 44-5 Jangchung-dong 1 (il)-ga, Jung-Gu, Seoul 100-391 (KR). YOON, Woong, Sup [KR/KR]; Ssang-yong Apt. 504-1202, 767 Muwonmaeul Haengsin-dong, Deonyang-gu, Goyang-si, Gyeonggi-do 412-220 (KR). LEE, Kwan, Young [KR/KR]; Sambu Apt. 1-122, 30 Yeouido-dong, Yeongdeungpo-Gu, Seoul 150-882 (KR). HWANG, Jung, Ho [KR/KR]; Dong-a

Green Apt. 106-1402, 411 Ichon-dong, Yongsan-Gu, Seoul 140-030 (KR). LEE, Kyo, Seung [KR/KR]; Korong Villa.2-302, 322-1 Hongeun 3-dong, Seodaemung-gu, Seoul 120-848 (KR). JEONG, Dong, Hoon [KR/KR]; Imaechon Apt. 605-1602, 123 Imae-dong, Bundang-gu, Seongnam-si, Gyeonggi-do 463-796 (KR). LEE, Hyeong, Sang [KR/KR]; Naksung-Hundae Apt. 102-902, 181-1 Bongcheon-dong, Gwanak-gu, Seoul 151-050 (KR). LEE, Dae, Won [KR/KR]; Jugong Apt. 312-907, Dunchon-dong, Gangdong-gu, Seoul 134-060 (KR). RYU, Jae, Hong [KR/KR]; Jinyang Apt. 1-1454, Chugmuro 4(sa)-ga, Jung-gu, Seoul 100-863 (KR).

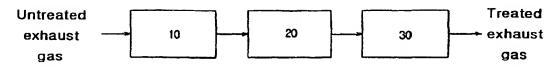
- (74) Agent: IM, Jae, Ryong; RM 502, New Seoul Building, 828-8, Yeoksam-dong, Kangnam-gu, Seoul 135-080 (KR).
- (81) Designated States (national): CA, CN, JP, US.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: APPARATUS FOR REMOVING SOOT AND NO_X IN EXHAUST GAS FROM DIESEL ENGINES



(57) Abstract: Disclosed is a plasma system for removing soot and nitrogen oxides (NO_x) in exhaust gas from diesel engine. Such system comprises a diesel particulate filter for accommodating a honeycomb type porous element and at lest one pair of electrodes; a plasma reactor for creating a predetermined amount of plasma, mounted downstream or upstream of said diesel particulate filter; a catalytic reactor filled with a catalyst selected from the group 1B metals, mounted downstream of said plasma reactor or said diesel particulate filter; and a hydrocarbon-feeding means for feeding hydrocarbon to exhaust gas, connected to an arbitrary position upstream of said plasma reactor. Therefore, soot and NO_x in the exhaust gas, which are components harmful to human beings, and are also pollutants, can be effectively removed at a normal pressure by use of such system.

1

APPARATUS FOR REMOVING SOOT AND NO_X IN EXHAUST GAS FROM DIESEL ENGINES

TECHNICAL FIELD

The present invention pertains to an apparatus for removing soot and nitrogen oxides (NO_x) in exhaust gas from diesel engines, in particular, to such a plasma/catalyst system.

5

10

15

20

25

PRIOR ART

Generally, diesel engines are advantageous in terms of hardly inducing global warming, owing to having higher heat capacity and durability and lower amount of exhausted CO, CO₂ and hydrocarbons than gasoline engines. However, nitrogen oxides (NO_x) in the exhaust gas from the diesel engines are found to cause photochemical smog, acid rain and ozone (O₃). In addition, soot particulates absorb much more light than any other particulates suspended in cities, so that they cause the atmosphere and visual field to be turbid, and also such particulates inhaled by people are adsorbed by the respiratory tract, thus causing respiratory diseases.

Techniques for treating exhaust gas from diesel engines are classified into methods for physically separating soot using a filter; for simultaneous removing soot and NO_x by oxidizing NO to NO₂ using a non-thermal plasma and then eliminating soot with NO₂; for oxidizing hydrocarbons or reducing NO_x with catalyst; and combinations or modifications thereof.

European Pat. EP0937870 to Delphi Co., discloses an apparatus for removing hydrocarbon, CO and NO_x by use of a plasma/catalyst system. In the apparatus, exhaust gas passes through a catalytic layer, a plasma reactor, and finally another catalytic layer. As such, hydrocarbon and CO are partially oxidized by O₂ and removed in the first catalytic layer, and NO is converted to NO₂ in the plasma reactor. Additionally, in the second catalytic layer, the remaining hydrocarbon and CO are removed by oxidation with NO₂ produced in the plasma reactor and also

2

with the catalyst.

5

10

15

20

25

30

PCT Pat. WO98/00221, U.S. Pat. Nos. 5,746,984 and 6,156,162 to Hoard, disclose an apparatus for treating diesel exhaust gas comprising a filter and a plasma reactor. The particulates collected in the filter are removed by oxidation with NO₂ produced in the plasma reactor placed in front of the filter. Ceramic, zeolite or perovskite coated with copper oxides or barium oxides are used as filter materials. The reaction time of the plasma and the regeneration time of the filter are determined by a sensor mounted in the outlet of the apparatus mentioned, and also by the increase of back pressure of the filter (or decrease of engine output). In addition, other various plasma reactors are disclosed.

U.S. Pat. Nos. 5,711,147, 6,038,853 and 6,038,854 to Penetrante et al., refer to a removal system of NO_x and particulates by 2-step processes. In the first step, after a plasma is generated in the presence of O₂ and hydrocarbon, NO is oxidized to NO₂, and the produced NO₂ is reacted with soot particles deposited on the filter and thus converted to N₂ or CO₂. In the second step, the remaining NO₂ passes through a catalytic layer in the presence of hydrocarbons, so being reduced to N₂. In particular, U.S. Pat. No. 6,038,854 discloses a reliable plasma/filter/catalyst system.

U.S. Pat. Nos. 4,902,487 and 5,943,857 and PCT Pat. WO 00/21646 to Johnson Matthey Co., disclose an aftertreatment system of exhaust gas comprising a catalyst and a diesel particulate filter. Particulates are first collected in the filter and then removed by oxidization with NO₂ at relatively low temperature, which is produced in the catalytic layer placed in front of the filter. A plasma reactor, instead of the catalyst, may be used. Then ozone (O₃) is additionally produced and thus allows soot to be oxidized.

PCT Pat. WO 00/43645 and WO 00/43102 to AEA Technology, refer to a removal method of particulates and NO_x using a plasma reactor and a catalyst. When a plasma is generated in the presence of hydrocarbons, NO is converted to NO₂, which then allows soot to be oxidized and thus removed. The remaining NO_x is removed by use of a catalyst. A dielectric barrier, instead of a filter, is dispersed between the electrodes.

PCT Pat. WO 00/29727 to Engelhard Co., refers to a NO_x (exclusive of

. 3

soot) removal system using a plasma reactor and a catalyst. This system allows NO_2 produced by a plasma in the presence of high concentration of hydrocarbon, to be reduced by use of the catalyst. It is described that, when a molar ratio of carbon atom in the exhaust gas to NO_x is 5:1, about 50 % of NO_x is converted to N_2 .

5

Ford Co., also reported that, when a molar ratio of NO_x to carbon atom in the exhaust gas is about 1:5 (the same ratio of the Engelhard Co.) in the presence of a plasma and a catalyst developed by the company itself, conversions of NO_x to N_2 and hydrocarbon to water or CO_2 are 50 % and 30 %, respectively.

10

In the International Symposium on High Pressure, Low Temperature Plasma Chemistry, held in Greifswald, Germany (September 10-13, 2000), Institute of Nonthermal Plasma Physics and Th. J. Heimbach GmbH, have disclosed an apparatus for removing soot, wherein, as can be seen in Fig. 1, a porous element 11 in which the soot is collected is used as one electrode, and other electrode 12a coated with dielectric barrier is inserted to the center of the filter cell to generate a plasma. Thus the filter cell itself is used as a plasma reactor, thereby removing the soot collected in the filter (HAKONE VII). In Fig. 1, NO in the exhaust gas is converted to NO₂ by the plasma generated between the porous element 11 and electrode 12 coated with dielectric barrier, present in the center of said porous element 11 electrode and the filter cell. When the produced NO₂ passes through the porous element 11 electrode, soot collected in the filter is oxidized and removed.

20

15

In any conventional systems for simultaneously removing soot and NO_x , NO in the exhaust gas is converted to NO_2 by the reaction as represented in the following reaction formula 1, and then soot and NO_2 are simultaneously removed by the reaction as represented in the following reaction formula 2. The remaining NO_2 is reduced to N_2 by the catalyst.

25

Reaction Formula 1
NO +
$$1/2 O_2 \rightarrow NO_2$$

Reaction Formula 2

C (soot) + NO₂
$$\rightarrow$$
 CO + NO or CO₂ + 1/2N₂

4

However, said reactions suffer from the disadvantage of incomplete treatment of soot in exhaust gas, because soot and NO_x-removing reactions occur only when NO₂-containing exhaust gas passes through a soot layer collected in the filter, and thus the reaction period of time is very short.

DISCLOSURE OF THE INVENTION

5

10

15

20

25

Therefore, an objective of the present invention for alleviating the problems as described above is to provide a plasma system for completely removing soot and NO_x in exhaust gas from diesel engines.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objectives, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

- FIG. 1 is a concept diagram showing a treatment system of exhaust gas from diesel engines developed by the Institute of Nonthermal Plasma Physics and Th. J. Heimbach GmbH.
- FIG. 2 is a schematic block diagram showing an apparatus based on one embodiment of the present invention.
- FIG. 3 is a concept diagram showing one embodiment of a diesel exhaust dust filter applied to Fig. 2.
- FIG. 4 is a concept diagram showing another embodiment of a diesel exhaust dust filter applied to Fig. 2.
 - FIG. 5 is a photograph of a diesel particulate filter after soot is removed.
- FIG. 6 is a graph of current and voltage flowing between electrodes in a soot-accumulated diesel particulate filter.
- FIG. 7 is a schematic block diagram showing an apparatus according to another embodiment of the present invention.
 - FIG. 8 is a concept diagram showing the main configuration of a plasma

5

reactor in Fig. 7.

FIG. 9 is a concept diagram showing the main configuration of a catalytic reactor in Fig. 7.

BEST MODES FOR CARRYING OUT THE INVENTION

5

A plasma system for achieving said objective of the present invention is classified into two aspects; one is that comprising a diesel particulate filter 10 for accommodating a honeycomb type porous element 11 and at least one pair of electrodes 12; a plasma reactor 20 for creating a predetermined amount of plasma, mounted downstream of said diesel particulate filter 10; a catalytic reactor 30 filled with a catalyst selected from the group 1B metals, mounted downstream of said plasma reactor 20; and a hydrocarbon-feeding means for feeding hydrocarbon to exhaust gas, connected to a critical position upstream of said plasma reactor 20.

15

10

The other aspect of the plasma system of the present invention is composed of a plasma reactor 20' for generating plasma from a supplied AC power source; a diesel particulate filter 10', connected downstream of said plasma reactor 20'; a catalytic reactor 30' for accommodating a predetermined catalyst, connected downstream of said diesel particulate filter 10'; and a hydrocarbon-feeding means for feeding hydrocarbon to exhaust gas, connected to a critical position upstream of said plasma reactor 20'.

20

With reference to Fig. 2, there is shown an apparatus according to one embodiment of the present invention. Fig. 3 shows one embodiment of the diesel particulate filter applied to Fig. 2, and Fig. 4 shows another embodiment of the diesel particulate filter applied to Fig. 2.

25

The diesel particulate filter 10, which is the most distinguished element in the system of the present invention, comprises a honeycomb type porous element 11, an electrode 12a inserted from the rear of the porous element 11, and an electrode 12b for totally shielding the porous element 11. Two electrodes are connected to a power supply 13, as in a conventional plasma reactor. So, when

6

soot is accumulated in the filter, electrical discharge occurs and thus the soot is burned out.

The present invention is based on the facts that a breakdown voltage is decreased when conductive materials are present between the electrodes 12a and 12b confronting each other, and that considerable amounts (about 50 %) of soot generated from the diesel engine is electrically conductive, like graphite. Comparing with the results obtained by the Institute of Nonthermal Plasma Physics and Th. J. Heimbach GmbH, the present invention is different in that the electrode is not inserted to every filter cell, instead the electrode is inserted from the rear of the porous element 11. The filter itself is not used, as one of electrodes and the regeneration chemistry is very different from said reaction formula 1.

5

10

15

20

25

30

In the form of electrodes, the electrode 12b can be substituted by another electrode 12a also inserted from the rear of the porous element 11. That is, as shown in Fig. 4, when a power is supplied between electrodes 12a, inserted from the rear of the porous element 11, the same effect can be obtained. The number of electrodes is not important, as long as the number is 2 or more.

The operation for removing soot in the diesel particulate filter 10 of the present invention is as follows.

(1) While a voltage is applied to two electrodes, the diesel exhaust gas continuously passes through the diesel particulate filter and thus soot is accumulated in the filter. For the soot-accumulated spots, the breakdown voltage is decreased, thereby creating dielectric barrier discharge (DBD).

As mentioned above, because the molecular structure of soot is identical to that of graphite having electric conductivity, the discharge-creating position and the breakdown voltage depend on the position and also the amount of soot being accumulated.

A mechanism in which the exhaust gas stream and the soot are filtered and accumulated in the diesel particulate filter is seen in Fig. 2.

(2) Once oxidation occurs at the soot-accumulated sites by discharge, the temperature is drastically increased and thus soot is spontaneously oxidized.

7

After removal all the accumulated soot, the breakdown voltage at the burned sites is increased again, thereby terminating discharge.

(3) However, the breakdown voltage is lowered again due to quantities of soot continuously being delivered. As such, the generation of the discharge causes the accumulated soot to be oxidized. The phenomenon after the burning is the same as described above.

5

10

15

20

25

30

More specifically, the following processes can explain a mechanism that the accumulated soot is oxidized.

(1) The breakdown voltage is decreased at the soot-accumulated sites, resulting in the discharge.

- (2) Once discharge is generated, some oxygen molecules in the exhaust gas are converted to two oxygen radicals, and some of the Oradicals are converted to ozone (O₃).
- (3) If soot is oxidized by ozone, it is spontaneously removed, and the breakdown voltage is increased, thus the discharge is stopped.
- (4) While the accumulated soot is transferred to the sites at which the breakdown voltage becomes decreased, said (1), (2) and (3) reactions continuously occur.

Accordingly, the system of the present invention does not remove soot by said reaction formula 2, and also does not generate the plasma in the diesel particulate filter 10 all the time, which is different from the apparatus of Heimbach GmbH. That is, in order to maintain the back pressure in the diesel particulate filter 10 at a suitable level (to generate discharge under the moderate back pressure), the potential between the electrodes should be appropriately maintained. If that happens, soot is removed by a sequence of discharge starting from the most soot-accumulated sites. Therefore, the back pressure in the diesel particulate filter 10 can be constantly maintained. Instead of the porous element 11, a ceramic monolith filter, a ceramic fiber filter, a metal filter and the like can be used. The electrode 12 inserted from the rear of the porous element 11 may be coated with insulator or not.

5

10

15

20

25

Different from the apparatus suggested by the Institute of Nonthermal Plasma Physics and Th. J. Heimbach GmbH, in the apparatus of the present invention, the electrode contacts with exhaust gas filtered through the porous element 11, and thus soot is not directly accumulated in the electrode. So, the non-coated electrode may be used.

In the plasma reactor 20, NO is converted to NO_2 in the presence of hydrocarbons. Additionally, soot is removed by the reaction as represented in above reaction formula 2. The remaining NO_2 is reduced to N_2 in the presence of a catalyst.

Hence, hydrocarbons are fed by any hydrocarbon-feeding means at a certain position before the plasma reactor 20. In this regard, the hydrocarbon-feeding means may be mounted between engine and diesel particulate filter 10 or diesel particulate filter 10 and plasma reactor 20. Hydrocarbons may be supplied

from unburned residual fuel, without an additional hydrocarbon-feeding means.

Hydrocarbons to be fed by the hydrocarbon-feeding means have 2-20 carbon atoms. In the absence of the hydrocarbon-feeding means, diesel engine fuel may be supplied.

The plasma reactor 20 of the present invention generates plasma by corona discharge, microwave radiation, UV radiation, radio frequency (RF) discharge, dielectric barrier discharge, glow discharge, surface discharge, or plasma jet. As such, as a power source to be supplied, use may be made of direct current, direct current pulse and alternating current.

In the catalytic reactor 30, the remaining NO₂ is removed as shown in the following reaction formula 3. Use is made of the catalyst selected from the group 1B, in particular, silver (Ag).

Reaction Formula 3 $NO_2 + hydrocarbon \rightarrow N_2 + CO_2 + H_2O$

9

Turning now to Fig. 7, there is shown an apparatus according to another embodiment of the present invention. Figs. 8 and 9 show main configurations of the plasma reactor and the catalytic reactor in Fig. 7, respectively.

The present apparatus comprises an AC power source-supplied plasma reactor 20', a diesel particulate filter 10' directly connected to said plasma reactor, and a catalytic reactor 30' filled with silver catalyst. A mixture of hydrocarbon and diesel engine exhaust gas to be treated passes through the plasma reactor 20', the diesel particulate filter 10' and the catalytic reactor 30' in order, thus removing soot and NO_x.

5

10

15

20

25

30

It is known that hydrocarbon favors the conversion of NO to NO₂. Accordingly, hydrocarbon may be fed by any hydrocarbon-feeding means placed in arbitrary positions before the plasma reactor 20', or may be supplied from unburned residual after the diesel fuel is burned in the engine, without an additional hydrocarbon-feeding means. At that time, hydrocarbons having 2-20 carbon atoms may be used.

The concrete configuration of the plasma reactor is seen in Fig. 8. The electrode 22 in which an iron sheet 21 coated with ceramic 21a such as alumina, is operated at a normal pressure with supplying energy of 10-100 J/L per unit flow of exhaust gas. The plasma reactor 20' does not fundamentally remove NO_x or soot, but performs conversion of NO to NO₂.

In the diesel particulate filter 10¹, soot in the exhaust gas is filtered and collected. The collected soot reacts with the NO₂ converted in the plasma reactor 20¹, and then is oxidized.

As one of silver catalysts is filled in the catalytic reactor 30 , Ag/Al₂O₃ catalyst prepared by incorporating aqueous AgNO₃ solution into γ -Al₂O₃ to sinter, is used. The catalytic reactor 30 is operated at 200-450 °C. In the catalytic reactor 30 , NO_x reduction reaction in which NO₂ and NO are reduced to N₂ occurs.

A better understanding of the present invention may be obtained in the light of the following examples which are set forth to illustrate, but are not to be construed to limit the present invention.

10

EXAMPLE 1

In a diesel particulate filter/plasma/catalyst system of the present invention, exhaust gas from a diesel engine (2.9 L, Carnival manufactured by Kia Motors, Korea) was passed through a diesel particulate filter 10, and thus soot was accumulated in the filter. While altering input frequencies, soot removal efficiency of the diesel particulate filter was measured.

A 10 kV AC power source as a power supply 13 was connected between electrodes 12a and 12b, and then a mixture gas of helium (90 %) and oxygen (10 %) was passed through the diesel particulate filter containing soot collected from the engine exhaust gas at a flow rate of 0.5 L/min at temperature (15 °C). By use of gas chromatography (not shown), concentrations of CO and CO₂ were measured. Other conditions are as follows.

- (1) Diesel particulate filter: outer diameter 47 mm, length 200 mm
- (2) Glass tube: inner diameter 47 mm, length 300 mm
- (3) Electrode: stainless rod (center electrode) having a diameter of 1 mm, and net made of iron (outside electrode)
- (4) Gas chromatography: YoungIn M600, Carboxen-1000 column, and TCD and FID detector.

During input frequency was altered to 60, 100, 200, 300 and 500 Hz, the concentrations of CO and CO₂ were measured. The results are given in Table 1, below.

TABLE 1

No.	Frequency (Hz)	CO (ppm)	CO ₂ (ppm)
11	60	396	69
2	100	642	120
3	200	1426	229
4	300	1625	325

15

20

10

5

	1.	L	
5	500	2107	437
5	500	2107	437

From the above table, the presence of CO and CO₂ implys that soot is oxidized. As the input frequency, that is, the energy density is increased; the concentrations of CO and CO₂ become higher.

Fig. 5 shows a photograph of the diesel particulate filter after soot is oxidized. In this drawing, it can be seen that the soot-removed portion is certainly distinguished from the soot-unburned portion. The white portion indicates that regeneration of the filter has been completed, and the relatively black outer portion shows portion, which is undergoing regeneration.

5

10

15

20

25

Fig. 6 shows the current flowing between the electrodes in the soot-accumulated diesel particulate filter. The current is measured at the frequency of 300 Hz, and the peaks mean momentary discharge. The average current when soot is not accumulated is 0.4-1.2 mA, which corresponds to 16-36 % of 2.5-3.3 mA when soot oxidation is occurring.

EXAMPLE 2

In a plasma/diesel particulate filter/catalyst system of the present invention, removal performance of NO_x were measured with a plasma reactor 20° and a catalytic reactor 30° by use of sample gas shown in the following table 2. The diesel particulate filter 10° was not additionally used. A glass filter 31 filled with glass wool within the catalytic reactor 30° was used. The catalytic layer was positioned after the filter layer. A NO_x analyzer (Thermo Environmental Instrument, Model 42H-not shown) was connected to the rear of each of the plasma reactor 20° and the catalytic reactor 30° , and thus concentrations of NO and NO_2 were quantitatively measured.

The plasma reactor 20' is a cylinder form having a diameter of 36 mm and a length of 300 mm. As energy, 60 Hz AC was supplied at a rate of 15 J/L per unit volume of sample gas.

12

As the catalyst, silver/alumina catalyst (Ag/Al₂O₃) was used and the reactor was operated at 250-500 °C.

TABLE 2

Component	NO (ppm)	NO ₂ (ppm)	O ₂ (%)	C ₃ H ₆ (ppm)	Atmospheric Gas
Sample Gas	495	-	10	1000	N_2

The concentrations of the gas after passing through the plasma reactor are shown in Table 3, below.

TABLE 3

Composition	Sample Gas	Exhaust gas in Plasma Reactor
NO conc. (ppm)	495	8
NO ₂ conc. (ppm)		450 .

As can be seen in the Table 3, most of NO is oxidized to NO_2 through plasma reaction. The reason why the total amount of NO and NO_2 is decreased by 37 ppm is that a small amount of NO_x may be removed in the plasma reactor, and also nitrogen compounds of other forms, not measured by the NO_x analyzer, may be produced.

10

15

In addition, it is assumed that soot can be removed, as represented in the above reaction formula 2.

With increasing the temperature of the catalytic reactor to 250 °C, 350 °C, 450 °C, experiments were carried out by use of sample gas passed through the diesel particulate filter/catalytic reactor (Fil/Cat), and the plasma/diesel particulate filter/catalytic reactor (Pl/Fil/Cat). The results of two cases are compared and shown in the following table 4.

13

TABLE 4

	25	0 °C	350 °C		450 °C	
Conc. (ppm)	Fil/Cat	Pl/Fil/Cat	Fil/Cat	Pl/Fil/Cat	Fil/Cat	Pl/Fil/Cat
NO	429	116	377	35	60	30
NO ₂	6	117	12	13	4	3
NO+NO ₂	435	233	389	48	64	33

From the table 4, it can be seen that the NO_x removal rate of the plasma/diesel particulate filter/catalyst system is much higher than that of the diesel particulate filter/catalyst over all temperature ranges. In particular, when the temperature of the catalytic reactor is 450 °C, the NO_x removal rate is the highest. In the case of using silver catalyst, activity of catalyst itself becomes better at relatively high temperatures. As can be shown in table 4, catalytic activity is significantly increased by plasma reaction.

5

10

15

20

Generally, the system having a good catalytic activity at low temperatures is favorably used as an automobile-mounting apparatus. At 350 °C, it is noted that the NO_x removal obtained by combination of plasma and catalytic reactions seems satisfactory.

INDUSTRIAL APPLICABILITY

By use of a diesel particulate filter/plasma/catalyst system or a plasma/diesel particulate filter/catalyst system of the present invention, soot and NO_x in diesel engine exhaust gas, which are components harmful to human beings, and are also pollutants, can be effectively removed at atmospheric pressure.

The present invention has been described in an illustrative manner, and it is to be understood that the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to

14

be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

15

CLAIMS

- 1. An apparatus for removing soot and nitrogen oxides in exhaust gas from diesel engines, comprising
- a diesel particulate filter or accommodating a honeycomb type porous element and at least one pair of electrodes;

5

15

20

25

- a plasma reactor for creating a predetermined amount of plasma, mounted downstream of said diesel particulate filter
- a catalytic reactor filled with a catalyst selected from the group 1B metals, mounted downstream of said plasma reactor; and
- a hydrocarbon-feeding means for feeding hydrocarbon to exhaust gas, connected to an arbitrary position upstream of said plasma reactor.
 - 2. The apparatus as defined in claim 1, wherein the electrodes in said diesel particulate filter comprise a rod type electrode inserted at the center of the passage section, and a pipe type electrode mounted to the outside of the passage section.
 - 3. The apparatus as defined in claim 1, wherein the electrodes in said diesel particulate filter comprise rod type electrodes, mounted in parallel at directly opposite positions of the passage section.
 - 4. The apparatus as defined in claim 1, wherein said plasma reactor generates a plasma by any method selected from the group consisting of corona discharge, microwave radiation, UV radiation, radio frequency (RF) discharge, dielectric barrier discharge, glow discharge, surface discharge, or plasma jet.
 - 5. The apparatus as defined in claim 1, wherein said plasma reactor uses any power source selected from the group consisting of direct current, direct current pulse and alternating current.

16

- 6. The apparatus as defined in claim 1, wherein said hydrocarbon-feeding means feeds hydrocarbon from an additional hydrocarbon-supplying source or from unburned residual after diesel fuel is burned in the engine.
- 7. The apparatus as defined in claim 1, wherein said hydrocarbons have 2-20 carbon atoms.
 - 8. An apparatus for removing soot and nitrogen oxides in exhaust gas from diesel engines, comprising
 - a plasma reactor for generating plasma from supplied AC power source;
 - a diesel particulate filter, connected downstream of said plasma reactor;
 - a catalytic reactor for accommodating a predetermined catalyst, connected downstream of said diesel particulate filter; and

10

15

- a hydrocarbon-feeding means for feeding hydrocarbon to exhaust gas, connected to an arbitrary position upstream of said plasma reactor.
- 9. The apparatus as defined in claim 8, further comprising a means for supplying hydrocarbon selected from the group consisting of propane, propylene, and diesel fuel, to diesel engine exhaust gas.
 - 10. The apparatus as defined in claim 8, wherein said plasma reactor is equipped with an electrode comprising an iron sheet coated with a ceramic layer, which is an insulator.
- 20 11. The apparatus as defined in claim 8, wherein said catalytic reactor is filled with silver catalyst.

1/5 FIG. 1

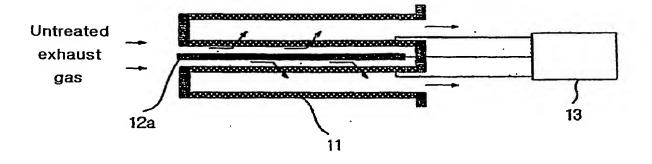


FIG. 2

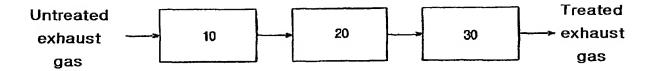
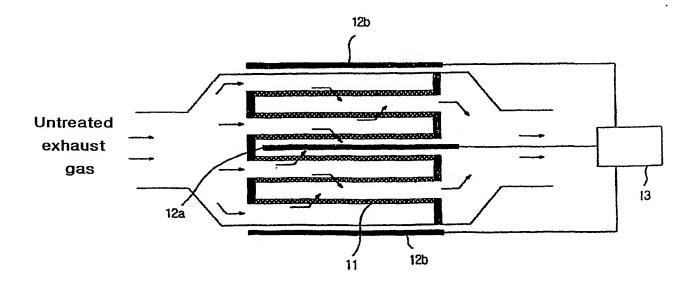


FIG. 3



2/5 FIG. 4

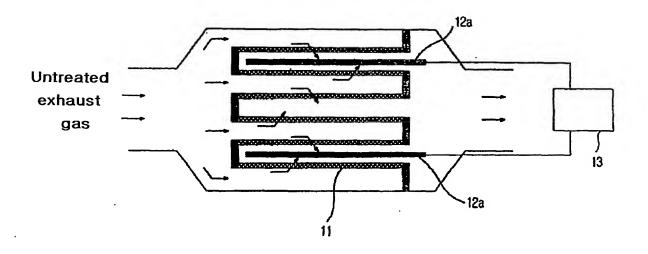
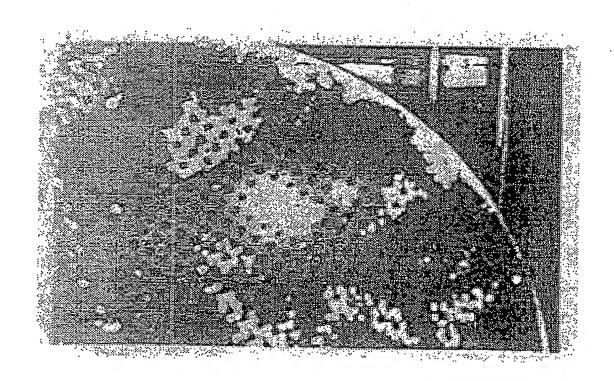


FIG. 5





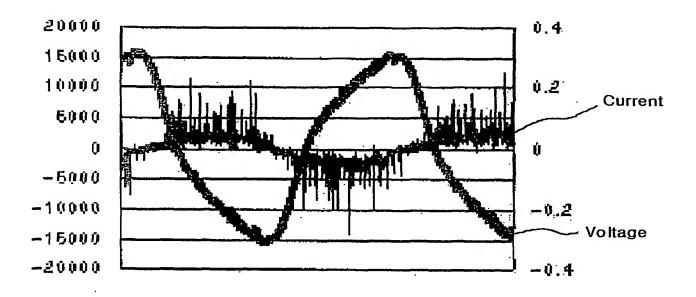
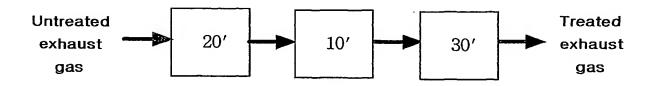
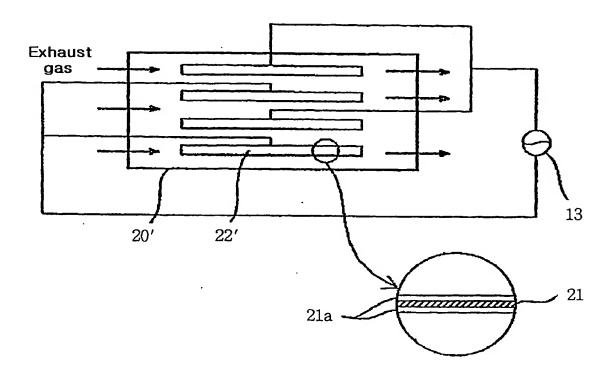


FIG. 7

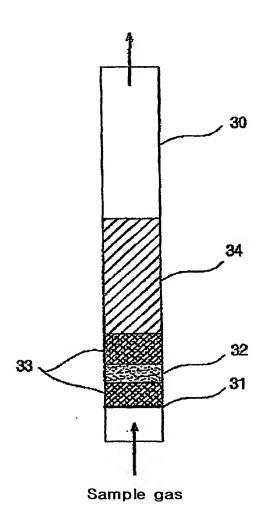


4/5

FIG. 8



5/5 FIG. 9



INTERNATIONAL SEARCH REPORT

International application No. PCT/KR01/00912

A. CLASSIFICATION OF SUBJECT MATTER				
IPC7 F01N 3/20C				
According to International Patent Classification (IPC) or to both national classification and IPC				
	mentation searched (classification system followed by	elassification symbols)		
IPC/ FUIN 3	/20, F01N 3/00, F01N 3/10		•	
Documentation	n searched other than minimun documentation to the e	extent that such documents are included in the	fileds scarched	
KOREAN PA	ATENTS AND APPLICATIONS FOR INVENTIONS	SINCE 1975		
	a base consulted during the intertnational search (name	e of data base and, where practicable, search t	rerms used)	
NPS, JPO				
			•	
C. DOCUM	MENTS CONSIDERED TO BE RELEVANT	· · · · · · · · · · · · · · · · · · ·		
Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.	
A	US 5,804,149 A (HOKUSHIN INDUSTRIES, INC.)	SEP. 8, 1998	1	
	CLAIMS AND FIGURE 1			
			_	
A	US 5,836,154 A (RAYTHEON COMPANY) NOV. CLAIMS AND FIGURE 1 TO 3	17, 1998	1 .	
Α	US 5,893,267 A (THE REGENTS OF THE UNIVE	RSITY OF CALIFORNIA) APR. 13, 1999	1	
1	CCLAIMES AND FIGURES	,		
	·			
			·	
			}	
			<u> </u>	
Further	documents are listed in the continuation of Box C.	See patent family annex.		
•	Special categories of cited documents: "I" later document published after the international filing date or prior document defining the general state of the art which is not considered date and not in conflict with the application but cited to understant.			
•	be of particular relevence the principle or theory underlying the invention		ion	
filing date	•			
cited to establish the publication date of citation or other "Y" document of particular relevence		step when the document is taken alone "Y" document of particular relevence; the claims	d invention cannot be	
special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other		considered to involve an inventive step whe		
means being of		being obvious to a person skilled in the art	ikiis,suui voimmattoii	
	published prior to the international filing date but later iority date claimed	"&" document member of the same patent family		
Date of the actual completion of the international search Date of mailing of the international search report		port		
22	22 OCTOBER 2001 (22.10.2001) 23 OCTOBER 2001 (23.10.2001)		1)	
	iling address of the ISA/KR	Authorized officer		
Government	ectual Property Office Complex-Daejeon, Dunsan-dong, Seo-gu, Daejeon	CHOL Joong II		
Metropolitan	City 302-701, Republic of Korea	Telephone No. 82-42-481-5418	Ville is it	

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS
M IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
FADED TEXT OR DRAWING
☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
☐ SKEWED/SLANTED IMAGES
COLOR OR BLACK AND WHITE PHOTOGRAPHS
☐ GRAY SCALE DOCUMENTS
☐ LINES OR MARKS ON ORIGINAL DOCUMENT
☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
OTHER.

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.